Alternate Lithography
-Soft and template based routes

Issues for research and education

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Outline

The Lycargus Cup "nanotechnology" of 4th century AD-

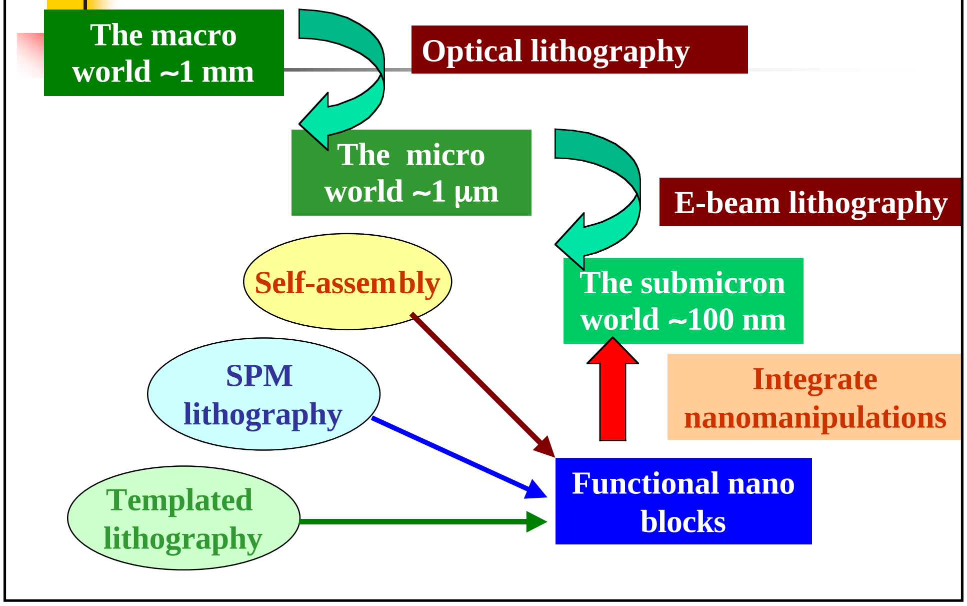
- Need for alternate lithography routes
- Some of the alternate routes
- Our activities and some results

Research and education – What are the issues in this area ?

A brief introduction to our group at Bangalore and Kolkata

- ✓ *Synthesis of nanomaterials by template based techniques*
- ✓ *Nano-fabrication using SPM like Dip-pen structures and nanomanipulation*
- ✓ *Noise and fluctuation in nanostructures*
- Application development with SPM and measurements with nanometer resolution
- The Physics of nanocrystal growth
- Biomolecular imaging using AFM and modeling of image
- Nanocalorimetry -application to DNA denaturation

Our strategy for Nano lithography and manipulations



The macro world ~1 mm

Optical lithography

The micro world ~1 µm

E-beam lithography

The submicron world ~100 nm

Integrate nanomanipulations

Self-assembly

SPM lithography

Templated lithography

Functional nano blocks

Alternate lithography :

- Si will remain the “main” material
- there are enormous scopes to add new features by alternate routes.

Complimentary route to standard CMOS –ULSI nanolithography

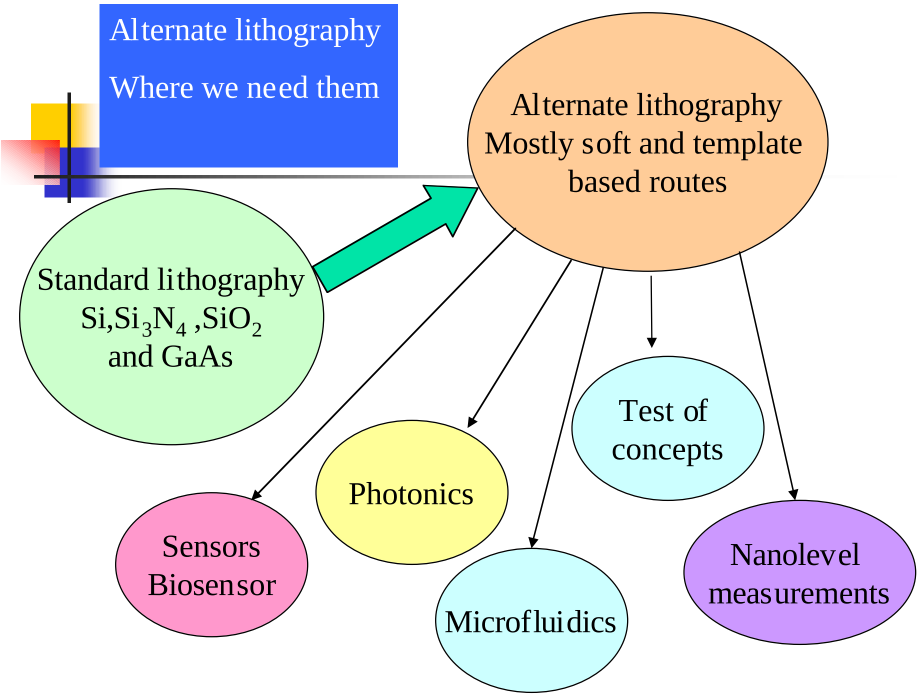
Principal Motivation

•Use of application specific functional materials to make nanomaterials and devices and integrate them with prefabricated structure (made by standard Lithography -optical, e-beam and FIB techniques)

•Can we integrate these two through a “seamless” route?

Alternate lithography

Where we need them



Alternate lithography Mostly soft and template based routes

Standard lithography Si, Si_3N_4, SiO_2 and GaAs

Sensors Biosensor

Photonics

Microfluidics

Test of concepts

Nanolevel measurements

Alternate lithography

Some major routes

Soft routes:

- Nanoimprint Lithography (NIL)-stamping on polymer.
- Microcontact Lithography-transferring a patterned SAM layer as a mask.
- SPM based methods-local anodic oxidation route,Dip pen lithography -creating a patterned SAM.
- Template based methods-membranes,block copolymer

Alternate lithography

Pros and cons

Main advantages:

1.Allows use of functional and biomaterials.

2.A quick way to test concepts.

3. Low cost and innovation driven.

Road blocks and challenges:

- Slow process and low throughput rate.
- Integration with CMOS processes.

Some examples of our work on synthesis using alternate routes

Growth of ABO_3 perovskite oxides-e.g,manganites,Titanates

The chemistry used-acetate/nitrate precursor, PEG medium

nanoparticles

a-SiO_2 substrate-nanostructered film

Template growth-nanowires and brush

Used as ink in Dip pen lithography-arrays of nanoparticles or wires on a substrate

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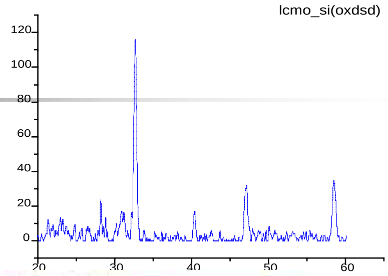
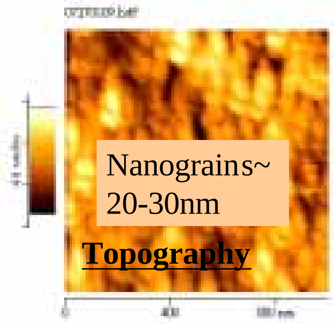
Nanostructered films of perovskite manganites showing large Piezoresistivity

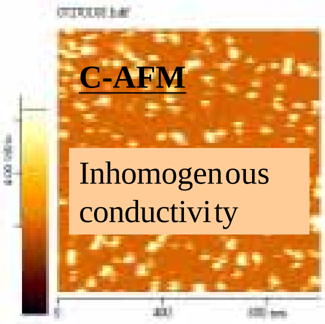


Chemical solution deposition on oxidized or RCA cleaned Si wafers



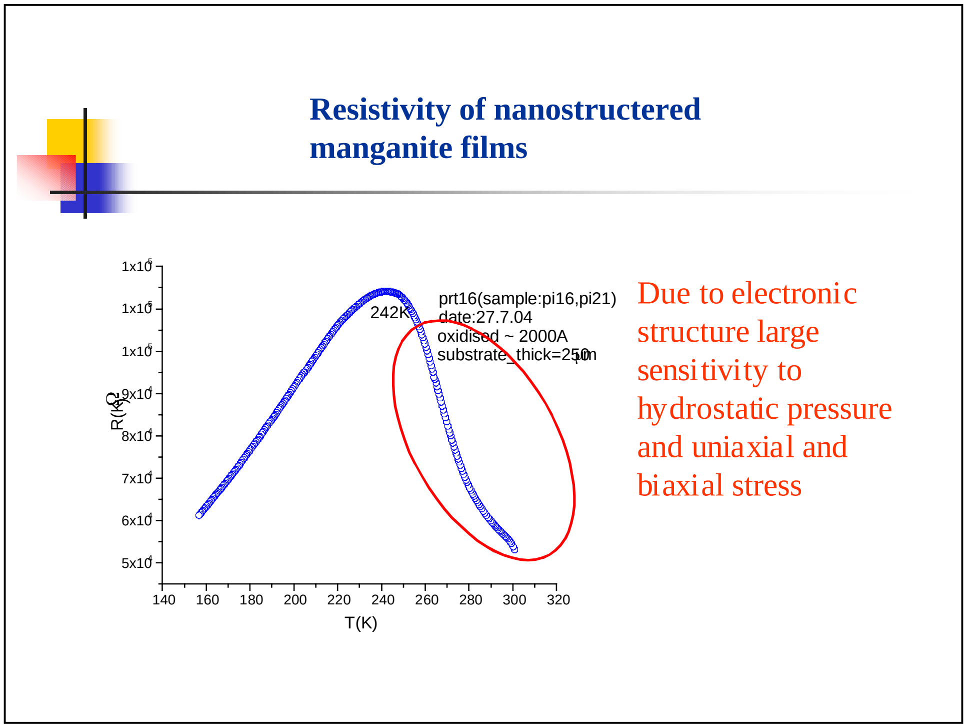
Nanograins~ 20-30nm

Topography



C-AFM

Inhomogenous conductivity



Resistivity of nanostructered manganite films

Due to electronic structure large sensitivity to hydrostatic pressure and uniaxial and biaxial stress

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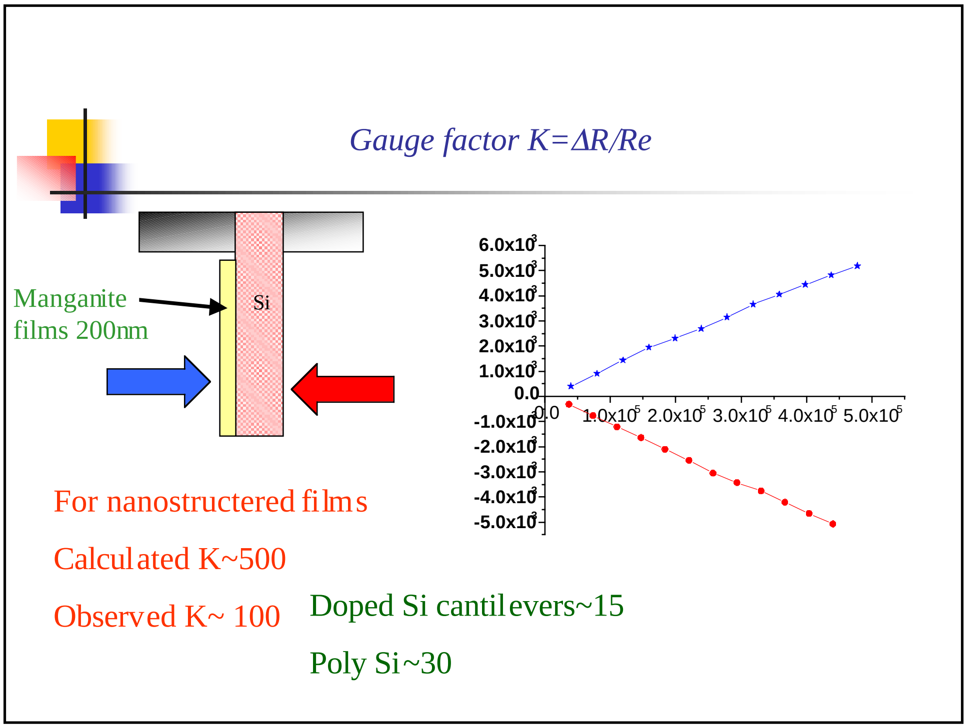


Gauge factor K=ΔR/Re

For nanostructered films

Calculated K~500

Observed K~ 100

Doped Si cantilevers~15

Poly Si~30

Translating that to an AFM cantilever

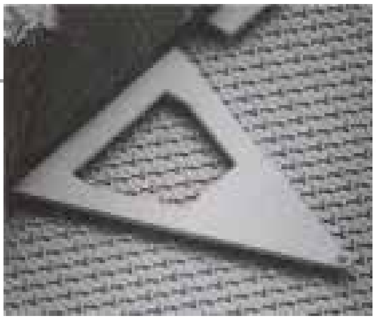
Cantilever Shape:Triangular

Length:200µm

Thickness: 0.4µm

k : 0.02N/m

Material: SiN



Tip displacement 10nm,force sensitivity 0.2nN

ΔR/R

Mangnite films~100 ppm

Piezo cantilever (commercial)~10-15ppm

Revisiting soft routes

Using Self Assembled layers

(SAM)

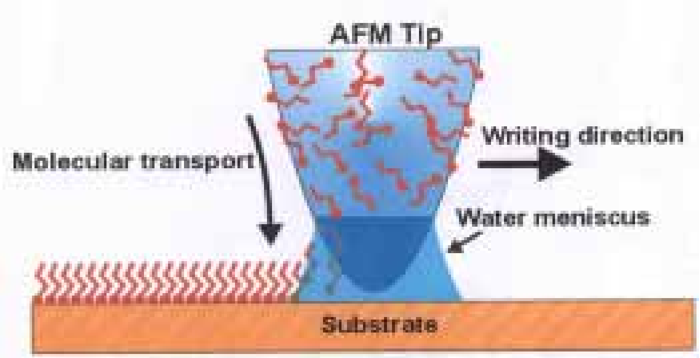
for pattern formation:

•Functional Materials form Dip-Pen Lithography

(DPN) route

Manganites and titatnates

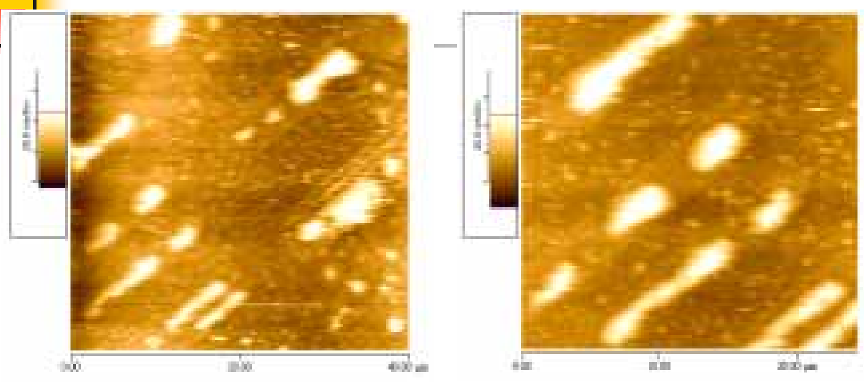
Basic concept of dip-pen lithography



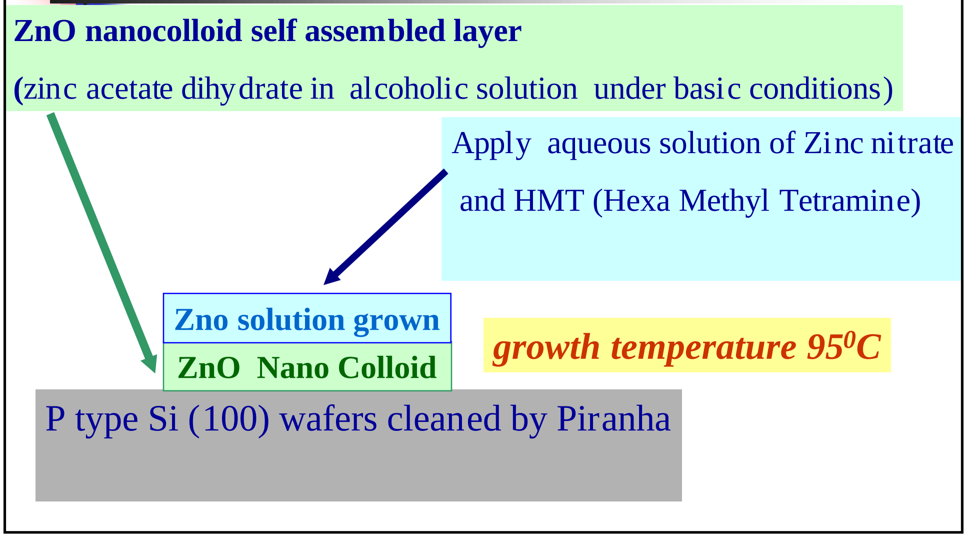
Mirkin et.al (2000)

- Transporting molecules from the tip to the substrate through the water meniscus
- Transferred layer forms a SAM
- Control- Humidity, hydrophilic or hydrophobic surface

LSMO on Si grown by DPN lithography



Growth of Oriented ZnO nano rods using self -assembled colloidal nano crystals as templates



ZnO nanocolloid self assembled layer

(zinc acetate dihydrate in alcoholic solution under basic conditions)

Apply aqueous solution of Zinc nitrate and HMT (Hexa Methyl Tetramine)

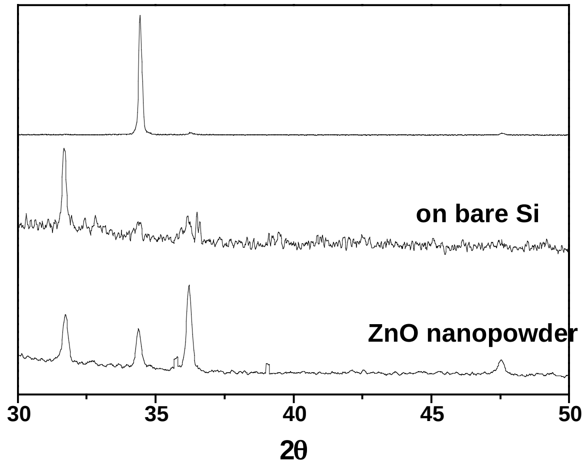
Zno solution grown

ZnO Nano Colloid

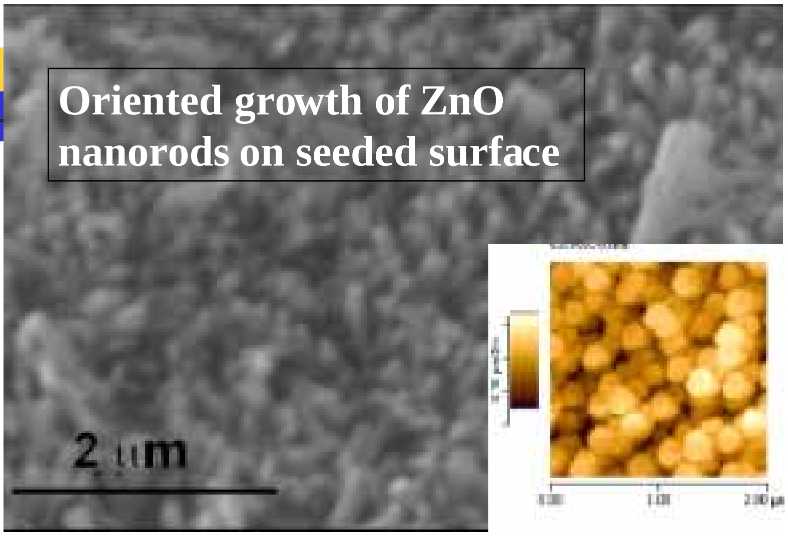
P type Si (100) wafers cleaned by Piranha

growth temperature 95^{0}C

XRD : Oriented growth of ZnO nanorods



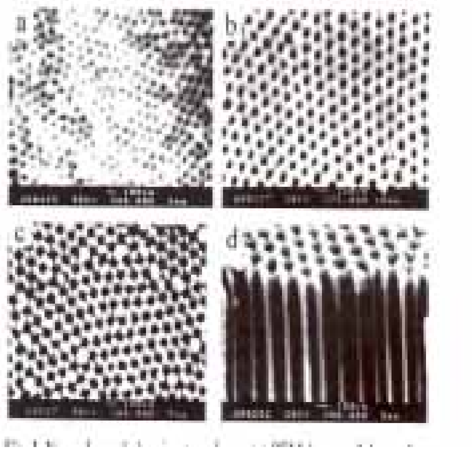
Oriented growth of ZnO nanorods on seeded surface



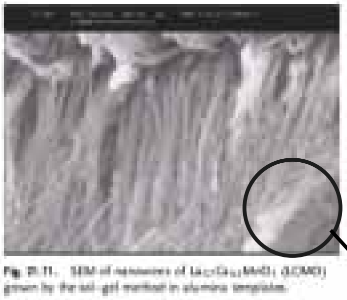
Average diameter
~240 nm

Synthesis of oriented oxide nanowires in alumina templates

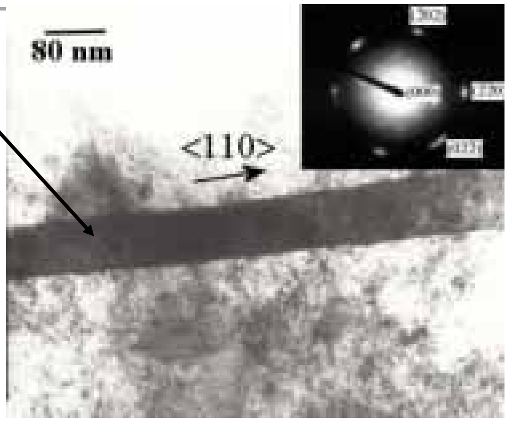
- Alumina made by anodic oxidation of Aluminium and subsequently etching the Aluminium
- Pore size ≥ 10 nm
- Length ~ few tens of μm
- High aspect ratio
- Can be grown on Si surface by oxidation of thick aluminum films



Raychaudhuri (2004)



Oriented growth of nanowires in templates

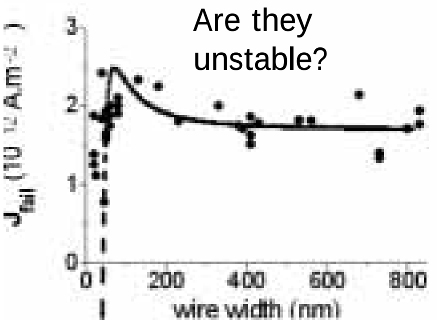


Directing the growth through the charge on the wall of the template

Shantha Shankar et.al Appl.Physics Letters (2004) ,Nanotechnology (2004)

Doing science with the template grown nano wires

How stable are metal nanowires when the diameter is below 50nm?



Are they unstable?

Experimental evidence on the Rayleigh instability of copper nanowires

M.E. Toimil Molares [a], A.G. Balogh [b], N. Chtanko [a], T.W. Cornelius [a], R. Neumann [a]

[a] Gesellschaft für Schwerionenforschung (GSI), Planckstr. 1, D-64291 Darmstadt
[b] Darmstadt University of Technology, Institute for Materials Science, Petersenstr. 23 [illegible]tadt, Germany

- Copper nanowires fabricated in etched ion track[illegible] of diameter 15nm, 30 nm and 60nm by electrodeposition.

Wires of diameter less than 60nm brea[illegible]pheres when annealed at high temperatures…typically aroun[illegible]

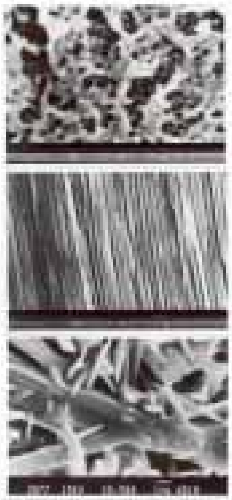
No such effect seen for wires of [illegible]arger than 60 nm.

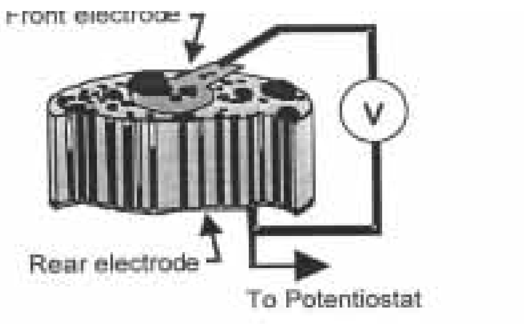
There are evidences that such wires with "magic" diameter can be stable

HRSEM image of 30 nm diameter copper wire after annealing under vacuum at (a) 400⁰C, (b) 500⁰C and (c) 600⁰C.

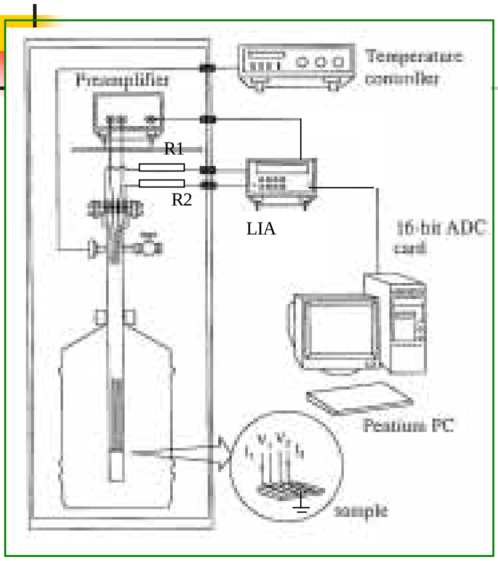
Noise spectroscopy with Ag Nano wires

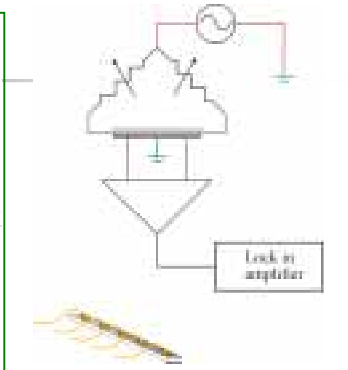
Electrochemically grown in alumina or polymeric templates





NOISE MEASUEMENT -A DSP BASED SYSTEM



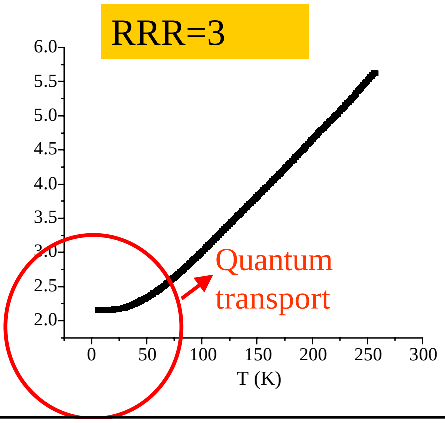


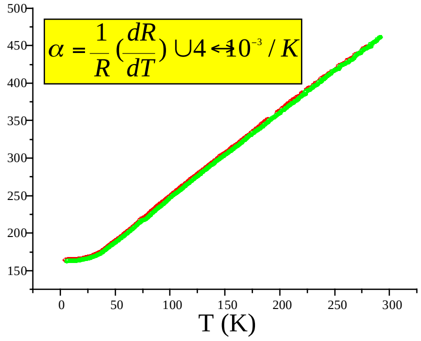
- Temeperature range 0.4K-500K
- Magnetic field upto 8T
- Noise floor S~$10^{-21}V^2$/Hz

Ghosh et.al (2004)

Electrical resistance of 15 nm Ag wires grown by templates

“Single” crystalline wire

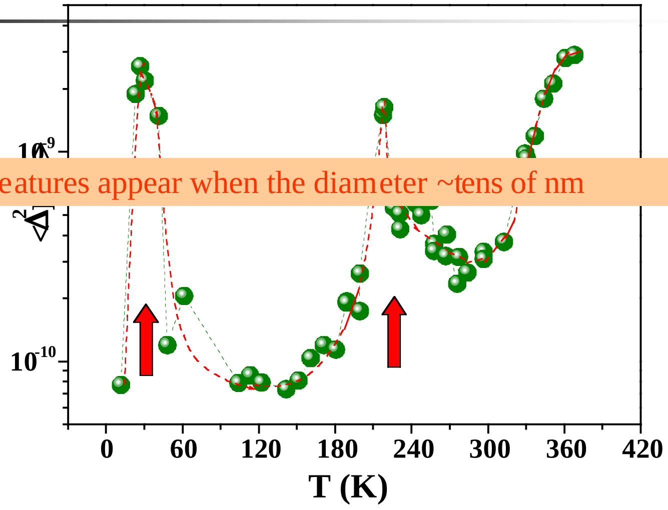




$$\alpha = \frac{1}{R}\left(\frac{dR}{dT}\right) \cup 4 \leftrightarrow 10^{-3} / K$$

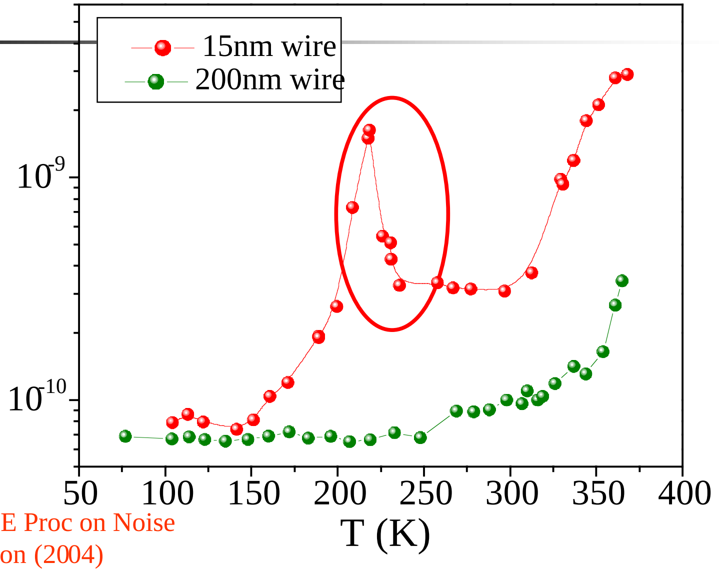
Bid et.al SPIE Proc on Noise and fluctuation (2004)

Relative fluctuation (integrated *S(f)* over band width) as a function of T



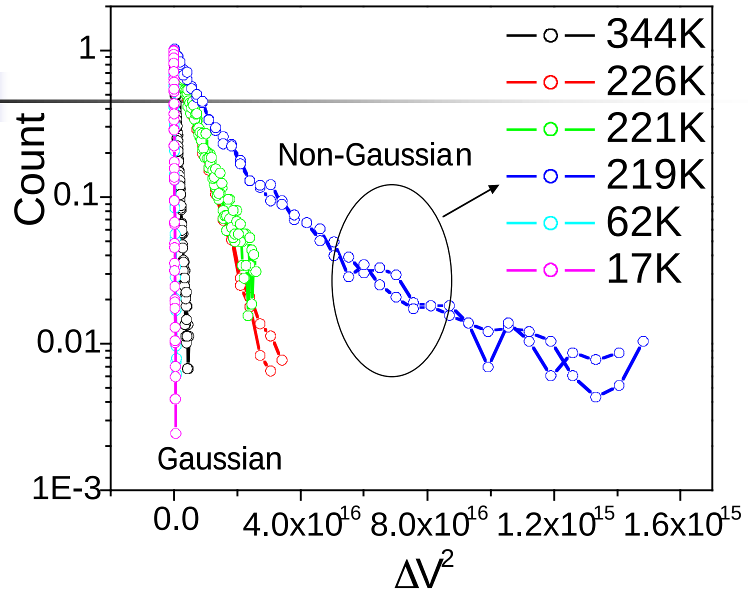
These features appear when the diameter ~tens of nm

Relative fluctuation (integrated *S(f)* over band width) as a function of T



Bid et.al SPIE Proc on Noise
and fluctuation (2004)

Probability distribution function of voltage jumps



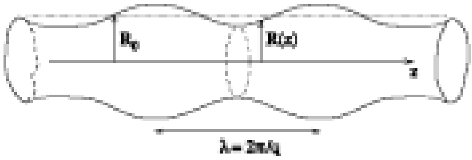
T > 100K -the classical regime

Observation of a temperature T^* at which the noise becomes large and non-gaussian.

•Onset of long range defect diffusion at $T^* \approx 220K < 300K$ this makes the nanowires unstable.

•Large instability at T^*-Rayleigh instability, which may be generic to nanowires.

Criterion of instability of a wire



If the fluctuations in the radius (r) of the wire has a wavelength (λ) greater than its circumference (i.e. $\lambda > 2\pi r$), the wire is unstable and tends to breakup into smaller segments to minimize its free energy (Plateau 1873)

Same criterion for the stability of a column of liquids (Rayleigh 1879) and of a solid cylinder considering mass transport by surface and volume diffusion (Nichols 1965).

$$R(z) = R_0(1 + \overset{\times}{\underset{0}{\square}} dq\, b(q)\cos(qz + \ddot{o}(q))$$

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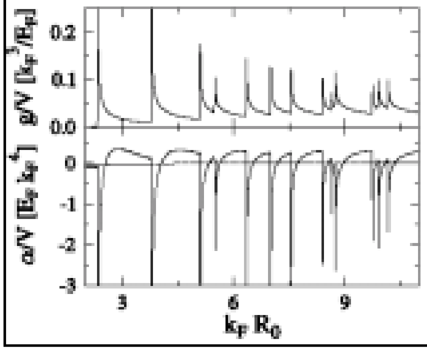
2. Ω when expanded to second powers of the fourier components b(q) gives

$$\Omega[b] = \Omega[0] + \int_0^{\infty} dq\, \alpha(q)[b(q)]^2 + \mathcal{O}(b^3).$$

There are fundamental reasons that will make a nanowire below a certain size susceptible to shape fluctuation due to large negative surface energy contribution



For the 15nm wire, $k_F R_0 = 90$

The wires show instability but they donot break.

What is T^* ?

The instability starts when there are sufficient mass transport

The instability can start at a low value of T/T_F

Issues for research and education

There are a number of issues of science in the areas of nanomanipulation and nanolithography that would not attention

1. For NIL- nanorheology and glass transition and polymer melting in constricted geometry.
2. Forces at nanoscale- the physics of nanomanipulation
3. Physics of crystal growth in constrained geometry
4. Bonding of templates and integration of template based growth to Si and
5. Integrating alternate lithography to CMOS processes

Acknowledgement:

My group; Shantha, Barnali, Loveleen, Aveek, Priya, Achyut, Sohini, Sai, Padma, Ravi, Jayanta

Collaborators:Prof. Dipankar Chatterjee

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- Department of Science and Technology

Thank You

- Defence Research and Development Organization
- Department of atomic energy
- Council of Scientific and Industrial Research
- Department of Biotechnology
- Department of Information Technology

Self-Assembly in biology

Self Assembled layers (SAM)

- Aligning and immobilizing DNA strands

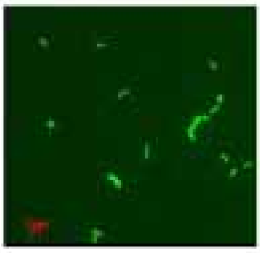
Long double stranded DNAs (ds DNAs) are immobilized on a monolayer of Zn-arachidate.

We have applied Langmuir-Blodgett technique to form the monolayer of Zn-arachidate where Zn (II) is bound to arachidic acid through charge neutralization.

Tetrahedral Zn (II) participates in DNA recognition through coordination,

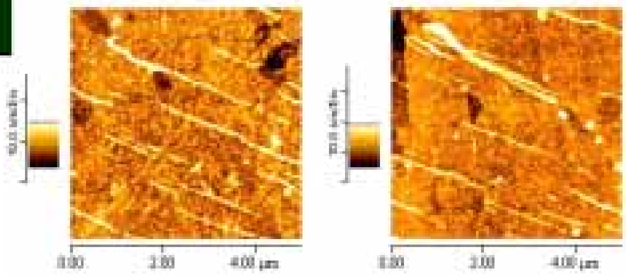
we have been able to layer DNA over the Zn-arachidate monolayer.

Noncontact mode images of DNA immobilized on a bilayer of HMDS and ZnA

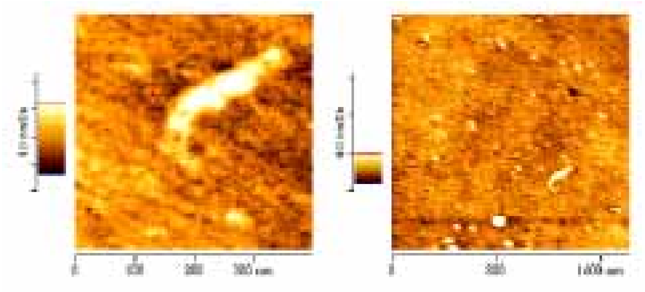


Florescence Image

DNA strands are visible on surface of 4 layer zinc arachidate.



Bhaumik et,al Langmuir (2004)



3kbps DNA on ZnA

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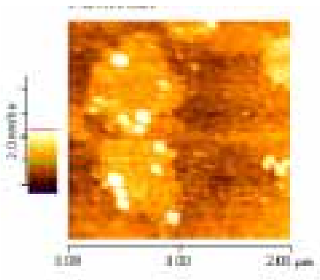
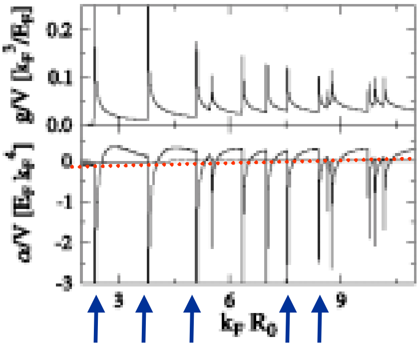
one layer of Zn-A + DNA + RNAp



Stability of a classically unstable wire



Density of states as a function of radius of the wire

The stability parameter α(q) as a function of radius of the wire.

The red dotted line shows the classical result based on surface tension and curvature energy for critical instability. The black line shows the result of full calculation taking into account the effect of electronic sub-bands .

Wires are very unstable for certain values of R as shown by arrows.

Note : ***As R increases beyond a certain value no more such instabilities come.***